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Effect of Charge Density Wave on Reflectance Spectra of TaS<sub>3</sub> and NbSe<sub>3</sub>(EXPERIMENTS ON MX<sub>3</sub> COMPOUNDS, International Symposium on NONLINEAR TRANSPORT AND RELATED PHENOMENA IN INORGANIC QUASI ONE DIMENSIONAL CONDUCTORS)

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Effect of Charge Density Wave on Reflectance  
Spectra of  $\text{TaS}_3$  and  $\text{NbSe}_3$

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We report the new reflectance results in the plasmon region of orthorhombic  $\text{TaS}_3$  (single crystal) as a function of temperature through the Peierls transition and in the near plasmon region of monoclinic  $\text{NbSe}_3$ , and the reflectivity at 1.96eV of both as a function of temperature. By the optical spectra we obtain the basic quantities for carriers and lattices. Further, we discuss the modification of one electron excitations and plasmon collective excitations through the new periodicity in crystals.

## I. Introduction

The electronic anomalies in the group-VB transition metal trichalcogenides have been attributed to the formation of charge density waves (CDW). During the past few years, a wide spread interest in the electrical, magnetic, superconducting and structural properties has evolved.<sup>1-5)</sup> Due to the difficulty in preparing samples wide enough for transmission or reflection experiments, there has been little experimental work on the optical properties of  $\text{TaS}_3$  and  $\text{NbSe}_3$ .<sup>6,7,8)</sup> These compounds are interesting system from the plasmon behavior. The electrons composing the plasmons are highly anisotropic in their electronic conduction which is considered to be quasi one dimensional, and two types of typical phase changes forming charge density waves are observed at low temperatures in these materials. Formation of CDW alters the electronic band structures, which includes the change in optical properties. Although the dynamical properties of CDW are extensively investigated, the information of basic physical quantities is poor. Optical reflection spectra are appropriate as a tool for studying the modification of the one-electron excitations and the plasmon collective excitations through the new periodicity

in crystals by the formation of CDW. We have made up the system measuring a reflection spectrum for wide energy region (0.45~3.1eV) of narrow samples ( $\sim 10\mu\text{m}$ ) at various temperatures.

In this paper we report the new reflection spectra in the plasmon region of orthorhombic  $\text{TaS}_3$  as a function of temperature through the Peierls transition and in the near plasmon region of monoclinic  $\text{NbSe}_3$ , and the reflectivity at 1.96eV of both as a function of temperature. Being analyzed in terms of simple Drude theory and Lorentzian dipole oscillator model, we determined the basic physical quantities for carriers and lattices. Further, we discuss the modification of the one-electron excitations and the plasmon collective excitations through the new periodicity in crystals.

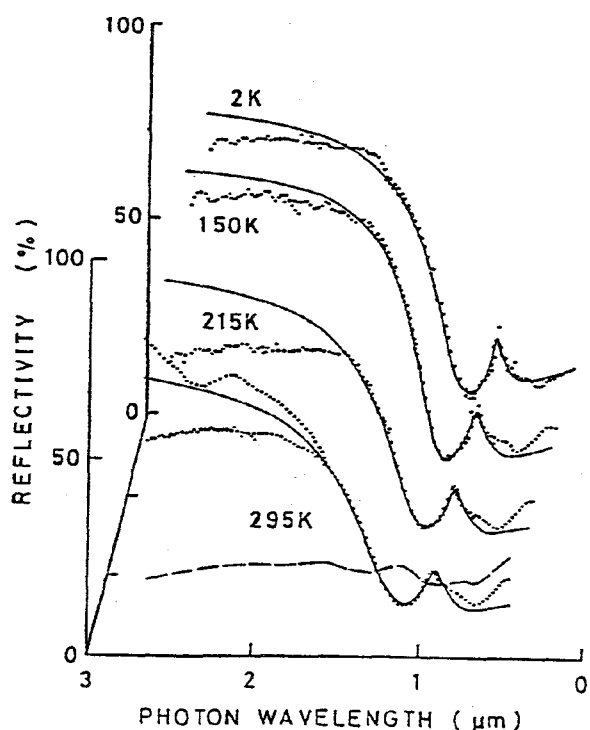


Fig. 1 Reflectivity of orthorhombic  $\text{TaS}_3$  at various temperatures as a function of incident photon wavelength. Dotted lines show the experimental results for the parallel polarization to the chain axis. Broken line shows the experimental result for the perpendicular polarization at R. T.. Solid lines show the best fit for the experimental results using Eq. (2).

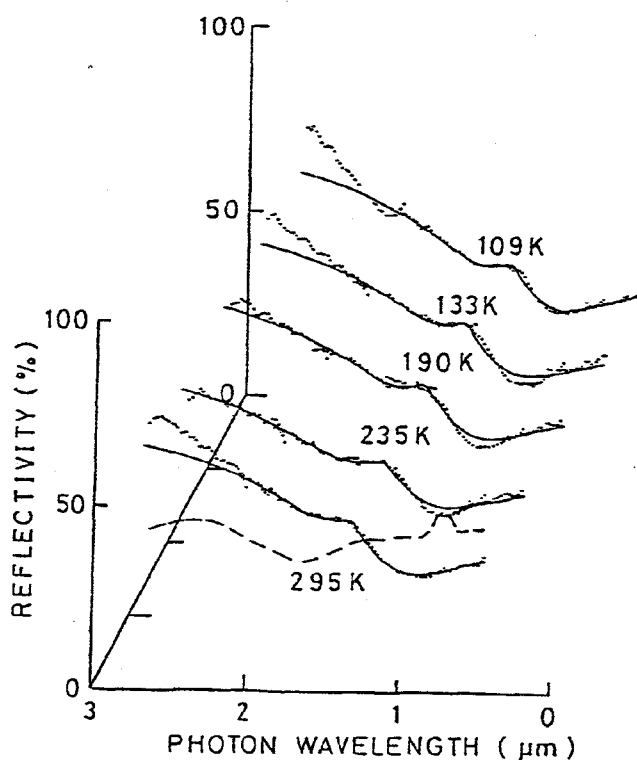


Fig. 2 Reflectivity of monoclinic  $\text{NbSe}_3$ . Dotted lines show the experimental results for parallel polarization. Broken line shows for perpendicular polarization. Solid lines show the best fit for the experimental results using Eq. (2).

## II. Experimental Results

Near normal reflectance on our samples (vapor-transport grown orthorhombic  $\text{TaS}_3$  and monoclinic  $\text{NbSe}_3$ ) was obtained by the system consisting of mirrors, a halogen lamp, a grating monochromator P-250 (Nikon) and two photo-conductive or photo-voltaic detectors (two paths and two detectors). The resulting reflectivities of  $\text{TaS}_3$  and  $\text{NbSe}_3$  for light polarized parallel and perpendicular to the conducting axis are shown as a function of temperature by dots and broken lines in Figs. 1 and 2. Figure 1 is of orthorhombic  $\text{TaS}_3$  and Fig. 2 is of monoclinic  $\text{NbSe}_3$ . The reflectance spectra for low temperatures ( $T < 295$ ) are lifted by  $n$  times 20% ( $n=1, 2, \dots$ ). The spectra show an expected anisotropic behavior at room temperature. The perpendicular reflectance shows no interesting structure for both compounds. The parallel reflectance, on the other hand, shows the structure of a plasma edge and an interband transition.

In Fig. 3, the spectra of the interband transition of  $\text{TaS}_3$  observed at 1.09eV (920nm) are shown as a function of temperature, and the energy of the main peak is plotted against temperature.

In Fig. 4, the reflectivity obtained at

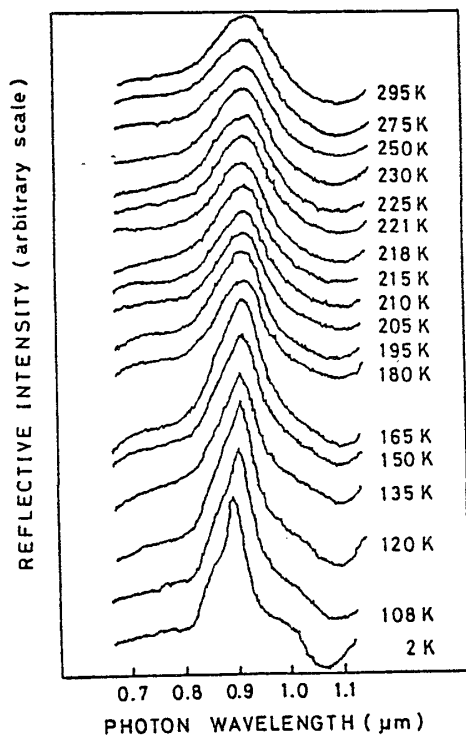


Fig. 3 Reflectance spectra of  $\text{TaS}_3$  near interband transition at various temperatures.

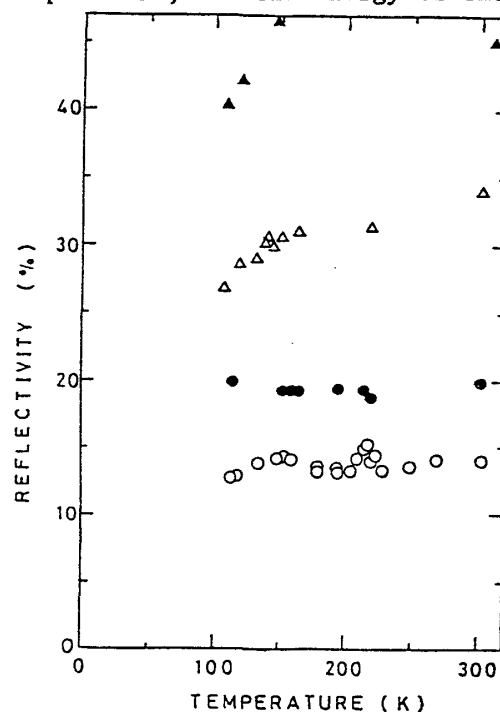


Fig. 4 Temperature dependence of reflectivity at 1.95eV.

$\text{TaS}_3$ : open circles for  $E//C$  and closed circles for  $E\perp C$  (orthorhombic).

$\text{NbSe}_3$ : open triangles for  $E//b$  and closed triangles for  $E\perp b$  (monoclinic).

1.96eV using a He-Ne laser is plotted against temperature for both compounds. We obtained the reflection spectra by connecting successively the spectra at various energy regions with the reflectivity at 1.96eV. By the subsequent connection there is much ambiguity at low energy region. We show two cases in observations of the reflection spectra at room temperature which are shown in Fig. 1.

### III. Discussion of Experimental Results

The reflectivities were fitted to the following

$$R = \frac{1 + \epsilon' - \sqrt{2} (\epsilon' + \epsilon_1)^{1/2}}{1 + \epsilon' + \sqrt{2} (\epsilon' + \epsilon_1)^{1/2}}, \quad (1)$$

where  $\epsilon' = |\epsilon_1 + i\epsilon_2| = (\epsilon_1^2 + \epsilon_2^2)^{1/2}$ .

We used the semiclassical dielectric function for a metal with one Lorentzian oscillator which is given by the following

$$\epsilon(\omega) = \epsilon\epsilon_0 \left( 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} - \frac{S\omega_i^2}{\omega^2 + i\omega\Gamma - \omega_i^2} \right), \quad (2)$$

where  $\omega_p^2 = ne^2/m_0m^*\epsilon\epsilon_0$ ,  $\epsilon\epsilon_0$  is the dielectric constant at high frequency arising from core polarizability,  $\tau$  is the electron relaxation time,  $\omega_p$  is plasma frequency,  $n/m^*$  is mass density,  $\omega_i$  is frequency of an interband transition,  $\Gamma$  is a width of the interband transition and  $S$  is oscillator strength. Equation (2) is applicable for anisotropic electron gas with anisotropic effective mass. It is considered that the effective mass is extremely anisotropic for  $\text{TaS}_3$ , because the plasma edge is not observed for perpendicular direction up to 0.5eV. It is estimated that  $m_{\parallel}/m_{\perp} < 0.1$ . The best fit at room temperature is obtained with the following parameter  $\epsilon = 5.4$ ,  $\omega_p = 1.17\text{eV}$ ,  $\tau = 1.7 \times 10^{-15}\text{sec}$ ,  $\omega_i = 1.34\text{eV}$ ,  $S = 0.09$ , and  $\Gamma = 0.3\text{eV}$  for orthorhombic  $\text{TaS}_3$ . The parameters derived by the above are  $V_F = 5.4 \times 10^8\text{cm/sec}$ ,  $n/m^* = 5.4 \times 10^{21}\text{cm}^{-3}$  and  $\sigma_0 = ne^2/m_0m^* = 2.6 \times 10^3 (\Omega\text{cm})^{-1}$ . For  $\text{NbSe}_3$ , the best fit at room temperature is obtained with the followings,  $\epsilon = 18$ ,  $\omega_p = 1.01\text{eV}$ ,  $\tau = 0.9 \times 10^{-15}\text{sec}$ ,  $\omega_i = 0.95\text{eV}$ ,  $S = 0.090$  and  $\Gamma = 0.3\text{eV}$ . Also  $n/m^* = 1.1 \times 10^{22}\text{cm}^{-3}$  and  $\sigma_0 = 2.7 \times 10^3 (\Omega\text{cm})^{-1}$  are calculated. For both compounds the estimated d.c. conductivity  $\sigma_0$  from their plasma edge is in good agreement with measured d.c. value along chain axis at room temperature. The Drude and one Lorentzian fit does not agree well with the experimental curve at low energy region where the absolute value is delicate because of

successive connections. Polarized single crystal reflection spectra were measured from  $0.4\mu\text{m}$  to  $2.6\mu\text{m}$  at various temperatures from 300K to 4.2K. The results were analyzed in the same way as for the room temperature data to find the optimum values of parameters. The results fitted to experimental data is shown in Figs. 1 and 2 by solid lines. First we discuss the results of  $\text{TaS}_3$  and next of  $\text{NbSe}_3$ .

a)  $\text{TaS}_3$  (orthorhombic)

The temperature dependence of the parameters is shown in Figs. 5 and 6.

In the high energy region where we observed the reflection spectra,

another interband transition seems to exist. The fitting is not good and the reflectivity is small there.

Then we assume that  $\xi$  is independent of temperature, but the results is not

almost changed by considering the dependence on temperature. The shift of plasmon energy is very sensitive to the absolute value of reflectivity.

Although the spectra are sensitive to samples and thermal hysteresis, which we could not study, exists on the optical properties, the results indicate the followings. The shift of plasma frequency sometimes shows hysteresis. Some of them have two anomalies in the temperature dependence (220K and 170K) and the other has also almost one anomaly (220K). Further the absolute reflectivity and the peak position of interband transition has two anomalies. The high temperature anomaly is always steep and clear at 220K but, the low temperature anomaly is a slight bend at 170K. Below the temperature of the lower anomaly, the interband transition at 920nm splits into three peaks (865, 899 and 1022 nm). Between the temperatures of two anomalies, the band width of the interband transition becomes broad. The width becomes sharp below the lower transition temperature. These results indicate that the anomalies are at the successive transitions due to a normal-incommensurate and an incommensurate-commensurate transition and show hysteresis effect. Below

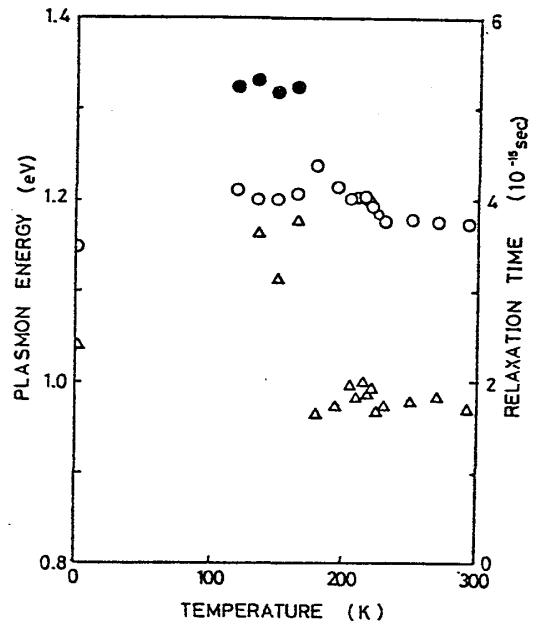


Fig. 5 Temperature dependence of plasmon energy (open circles) and its relaxation time (triangles) determined from the best fit of  $\text{TaS}_3$ . Closed circles show the hysteresis in plasmon energy.

the transition temperature, the electronic bands are folded by the new periodicity in crystals forming CDW. By the folding effect, the conduction band in normal state splits and Peirls gap appears at the Fermi energy. When we assume an average gap  $\omega_g$  between the new excited states and the filled band below the Fermi energy the dielectric constant becomes following

$$\epsilon^* = \epsilon \epsilon_0 \left( 1 - f \frac{\omega_p^2}{\omega^2} + \frac{(1-f)\omega_p^2}{E_g^2 - \omega^2} \right), \quad (3)$$

where we neglect the relaxation of electrons, interband transitions ( $\zeta = \infty$ ,  $s = 0$ ) and plasmon dispersion.<sup>9,10</sup> The factors  $f$  and  $1-f$  are required by generalized  $f$ -sum rules.<sup>11</sup> We get the plasmon energy under the new periodicity with an average energy gap  $E_g$  by resolving  $\epsilon^* = 0$  as followings,

$$\omega^2 = \omega_p^2 + \frac{1}{2} \left\{ E_g^2 - \omega_p^2 + \left[ (E_g^2 + \omega_p^2)^2 - 4(1-f)E_g^2\omega_p^2 \right]^{1/2} \right\}. \quad (4)$$

By the formation of energy gap and assuming  $f = 0$ , the plasmon energy changes to the effective one  $\omega_p^* = (E_g^2 + \omega_p^2)^{1/2}$ . The observed blue shift in plasmon energy shown in Fig. 5 is 0.03eV near 220K and the average gap  $E_g$  is determined to be 0.26eV. The physical quantities determined from the reflectivity by fitting is scattered below 170K. The scattering of the data is due to hysteresis effect.

Decreasing temperature the width of the interband transition at 1.34eV by the fitting becomes broad near the temperature of the Peierls transition (220K) and below 170K the peak of the reflection spectra separates into three peaks. Further the anomalies are also observed at 170K and 220K in the temperature dependences of

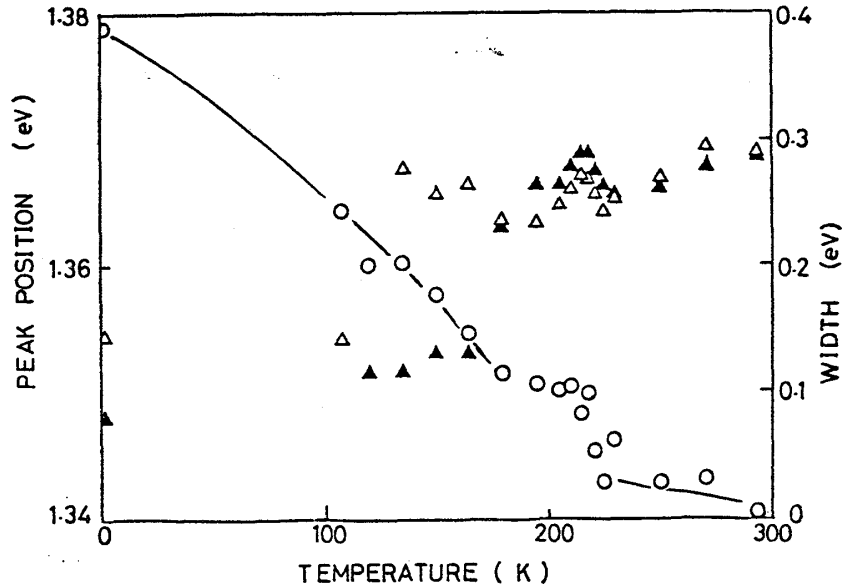


Fig. 6 Open circles and triangles (open and closed) show the temperature dependence of the peak energy and the width of the interband transition in reflectance spectra of  $\text{TaS}_3$ , respectively.

reflectivity at 1.959eV, the peak position of the interband transition, the plasmon energy and the relaxation time. These results also indicate that the higher temperature anomaly is normal-incommensurate and the lower one is incommensurate-commensurate transition.<sup>12)</sup>

The relaxation time of plasmon becomes long at the transition temperature decreasing temperature, but the change is not consistent with the transition.

#### b) NbSe<sub>3</sub>

The number of carriers in NbSe<sub>3</sub> is estimated by galvanomagnetic data, noise measurement, and cyclotron resonance study, but the disagreement between the estimates exists.<sup>1,2,6)</sup>

By a reflectance measurement, we try to estimate the carrier density (or mass density) near infrared region. In case of NbSe<sub>3</sub>, the reflectance edge is not so clear as of TaS<sub>3</sub>. Only we observe a tail, but we assume that the edge is due to a plasma edge and analyze the reflectance

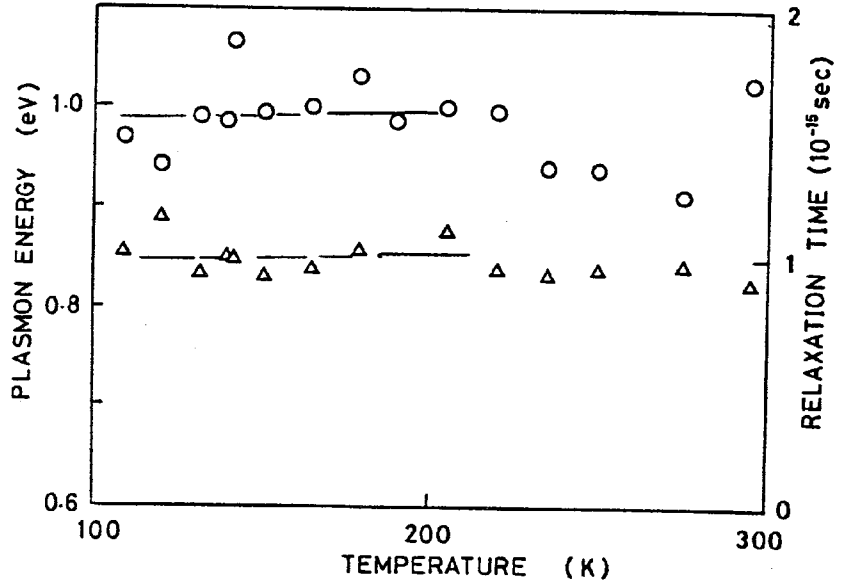


Fig. 7 Temperature dependence of plasmon energy (open circles) and its relaxation time (triangles) determined from the best fit of NbSe<sub>3</sub>.

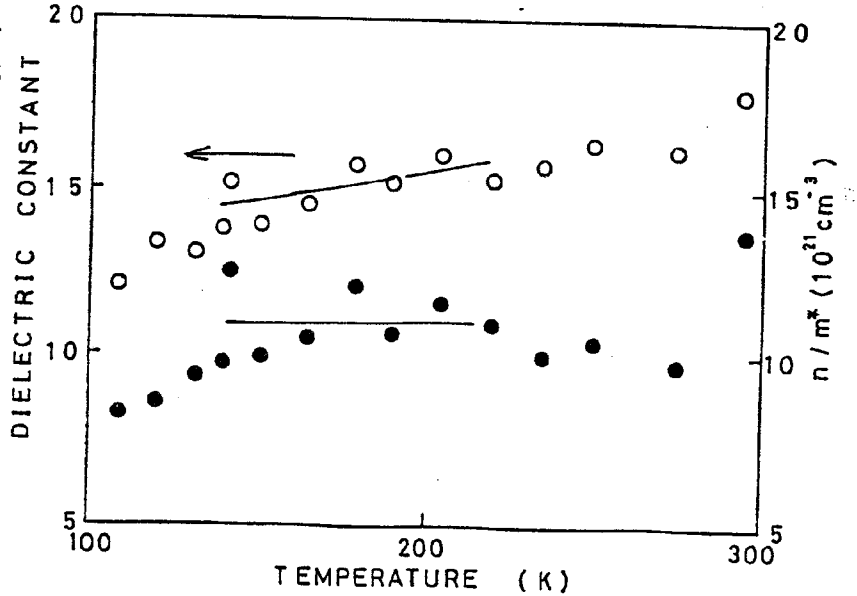


Fig. 8 Open Circles show dielectric constant  $\epsilon(\infty)$ . Closed circles show the mass density  $n/m^*$  calculated from  $W_p$  and  $\epsilon(\infty)$  for NbSe<sub>3</sub>.



spectra. By fitting we obtain the physical quantities similarly to  $\text{TaS}_3$ . The reflectivity is large in a higher energy region and we observe no peak except one interband transition near the edge. We can determine  $\xi(\infty)$  more precisely in  $\text{NbSe}_3$  than in  $\text{TaS}_3$ . The parameters are shown in Figs. 7 and 8, and the derived mass density from plasmon energy and dielectric constant is also shown in Fig. 8. The plasmon energy does not change through the higher CDW transition temperature but the mass density decreases below this transition temperature. The decrease in carrier number is due to the formation of CDW, which is same order as being estimated from the noise experiment.<sup>2)</sup> In this case the oscillator strength transfer  $f$  appeared in Eq. (3) is considered to be almost unity, but now we cannot estimate it by other knowledge. In conclusion, the present investigation and detailed analysis of the plasma edge provide the knowledge of basic physical quantities and phase change in  $\text{TaS}_3$  and  $\text{NbSe}_3$ .

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